

Flush-out of evaporitic sulphate salts in the Tinto River: Environmental implications

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The Tinto River drains one of the largest massive sulphide provinces in the world, the Iberian Pyrite Belt (IPB). As a consequence of intense mining activities dating back to the Third Millennium B.C., this river is extremely polluted by acid mine drainage (AMD) and releases a significant contaminant load into the 'Ría de Huelva' estuary [1].

During dry periods, the formation of evaporitic sulphate salts (mainly Fe sulphates) on riverbeds and AMD sources may play a key role in metal and acidity storage in the Tinto system. However, upon dissolution by rainfalls these highly soluble salts may release a high load of metal and acidity to an already polluted environment [2]. Water quality variations were monitored in October 2005 with an autosampler to study these flush-out processes in the Tinto catchment.

First rainfalls recorded in autumn in the Tinto catchment flushed out highly-soluble sulphate salts massively deposited during the summer. This flush-out event in October 2005 provoked a strong increase in sulphate (from 1964 to 8669 mg/L) and metal concentrations (from 199 t 1280 mg/L of Fe, from 88 to 462 mg/L of Al, from 17 to 113 mg/L of Cu, from 20 t 137 mg/L of Zn, etc.). Once these highly-soluble salts were washed out from riverbeds and spoil heaps, concentrations decrease progressively, reaching slightly higher values than those reached before rainfalls. However, elements such as Fe, As, Cr and Pb increased their concentration, being this increase especially significant for As (from 353 to 1885 µg/L). This increase could be due to dissolution of less-soluble salts releasing these elements into the river water. The dissolution of soluble salts with the arrival of the first rainfall after a long dry period provokes a yearly pulse of pollution into the Tinto River that may cause a significant damage to the living biota of the "Ría de Huelva" estuary.

[1] Ollás *et al.* (2006) *Appl. Geochem.* **21**, 1733-1749. [2] Cánovas *et al.* (2008) *Jour of Hydrol.* **350**, 25-40.

Overview of the geochemical modeling on CO₂ capture & storage in Italian feasibility studies

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CO₂ Capture & Storage in saline aquifers is presently one of the most promising technologies for reducing anthropogenic emissions of CO₂. In these sites the short-long-term consequences of CO₂ storage into a deep reservoir can be predicted by numerical modelling of geochemical processes.

Unfortunately a common problem working with off-shore closed wells, where only the well-log information are available, is to obtain physico-chemical data (e.g. petrophysical and mineralogical) needed to reliable numerical simulations. Available site-specific data generally include only basic physical parameters such as temperature, pressure, and salinity of the formation waters.

In this study we present a methodological procedure that allows to estimate and integrate lacking information to geochemical modelling of deep reservoirs such as: *i*) bulk and modal mineralogical composition, *ii*) porosity and permeability of the rock obtained from heat flow measurements and temperature, *iii*) chemical composition of formation waters (at reservoir conditions) prior of CO₂ injection starting from sampling of analogue outcropping rock formations.

The data sets in this way reconstructed constitute the base of geochemical simulations applied on some deep-seated Italian carbonatic and sandy saline aquifers potentially suitable for geological CO₂ storage.

Numerical simulations of reactive transport has been performed by using the reactive transport code TOUGHREACT via pressure corrections to the default thermodynamic database to obtain a more realistic modelling.

Preliminary results of geochemical trapping (solubility and mineral trapping) potentiality and cap-rock stability as strategic need for some feasibility studies near to be started in Italy are here presented and discussed.